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GB 1543014
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(54) **Ionising organic substances for mass spectroscopy**

(57) The use of mass spectroscopy of negative ions produced by laser beams, to analyse organic substances. Pulsed laser beams are focused by a lens 7 onto a solid sample 8 of the organic substance in a vacuum chamber 1. Negative ions are attracted by an electrode 9 and pass to a time of flight mass spectrometer. Liquid samples are transported through the focused beam of a laser on a transporting strip (15) Figure 2.

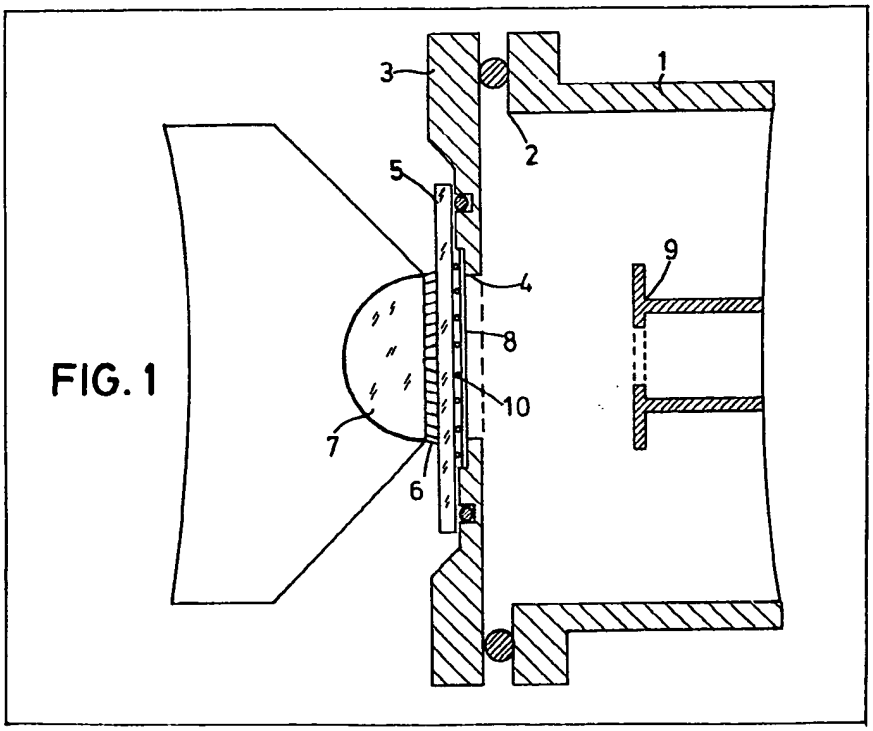

FIG. 1

The drawing(s) originally filed was/were informal and the print here reproduced is taken from a later filed formal copy.

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FIG. 1

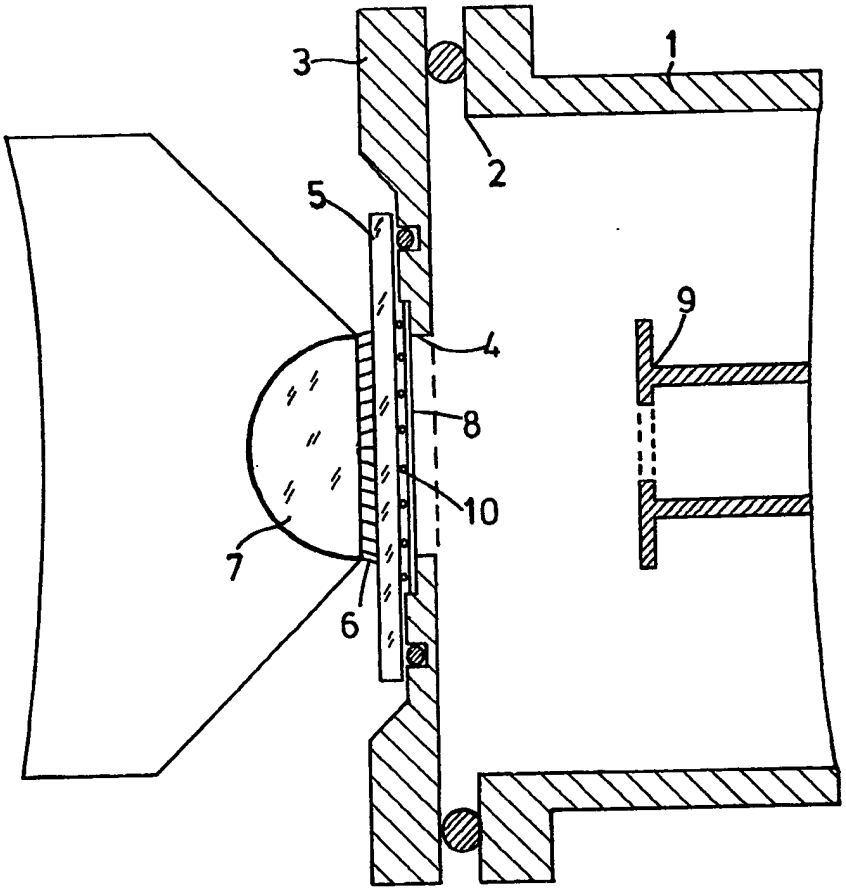
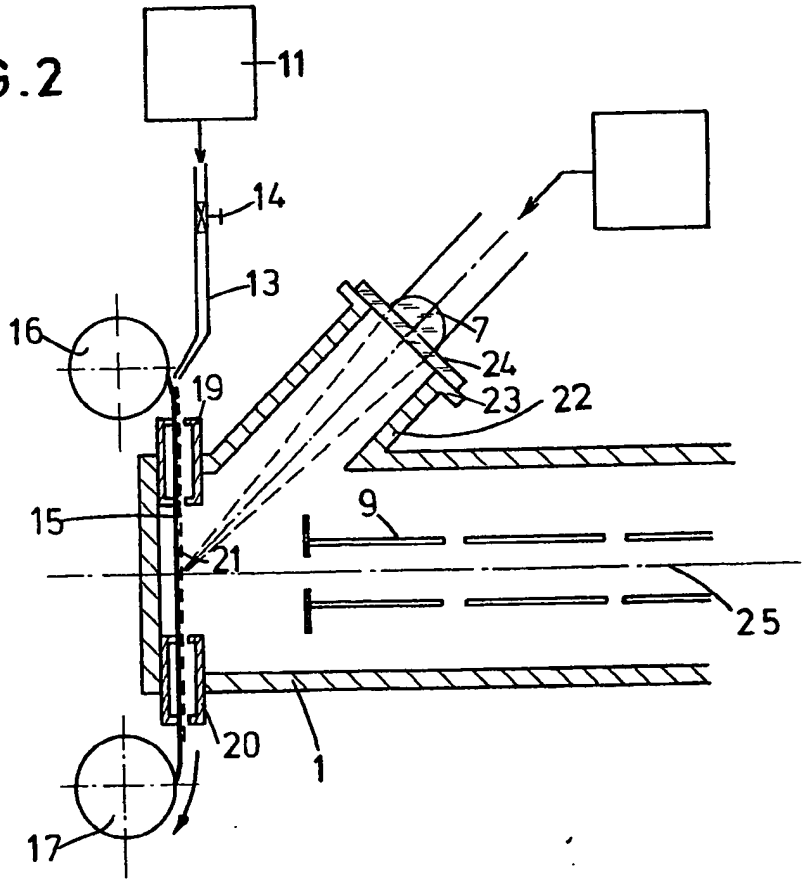


FIG. 2



SPECIFICATION

Analysis of organic substances

This invention relates to a method and apparatus for analysing organic substances.

The analysis of organic substances is particularly difficult because information has to be obtained not only on the atoms of which the molecules are composed, but also on the molecular structure.

From German Auslegeschrift 26 54 057 it is known to ionise the eluate leaving a liquid chromatograph and consisting of the carrier liquid and an organic substance dissolved therein, directly on a transporting strip or transporting wire, e.g. by applying a powerful electric field or by ion bombardment, and to investigate the resultant ions using a mass spectrometer. This procedure is intended to prevent a premature destruction of the molecular structure, such as occurs for example after evaporation and subsequent electron impact ionisation of the substance to be investigated. This method requires a solution, in the carrier liquid of the liquid chromatograph, of the substance to be investigated, and is thus unsuitable for analysing solid organic substances. Furthermore, the ionisation caused by ion bombardment or by the application of an electrid field produces a non-reproducible destruction of the molecular structure, with the result that it is difficult to draw conclusions concerning the starting substance from the mass spectra thereby obtained and essentially derived from molecular fragments, especially as the number of mass lines is increased further on account of multiple ionisations. With increasing mass number of the molecules to be investigated, the number of lines obtained therefore rises to such an extent that the analysis of organic substances, whose molecules have relatively high mass numbers (e.g. 200) is no longer possible.

The object of the present invention is to provide a method for analysing organic substances which will also make it possible to analyse organic substances having particularly large molecules and in which the evaluation of the mass spectra obtained is not complicated as a result of multiple ionisation.

In accordance with the invention, this objective is achieved by employing mass spectroscopy of negative ions produced by laser beams in order to analyse the organic substances.

Surprisingly, organic substances can be analysed in a particularly simple manner using this method, even if the molecules have mass numbers of 1000 and above. This is completely unexpected because in principle it has been assumed that linear organic molecules would be very largely disintegrated by laser beams. The mass spectra obtained with the aid of the method according to the invention do, of course, also show lines from fragments of molecules of the substances being investigated. These lines are, however, reproducible, and are thus always derived from fragments forming particular groups within the molecular structure. These lines can therefore also be used to provide information about the molecular structure.

A further advantageous feature is the fact that in the analysis of organic substances by the method according to the invention, no doubly charged molecule ions, or only a negligibly small number, are formed, and accordingly unequivocal and reproducible results can be obtained.

Further advantages and details of the invention will appear from the following description, reference being made to the accompanying generally schematic drawings, in which:-

Figure 1 is a sectional view of an apparatus for carrying out the analysis method according to the invention in the case of solid samples, and

Figure 2 is a sectional view of an apparatus for carrying out the analysis method according to the invention in the case of liquid or gaseous samples.

The apparatus shown in Figure 1 comprises a housing 1 having an opening 2 sealed in a vacuum-tight manner by a cover flange 3. The cover flange 3 itself also has an opening 4 which in its turn is sealed in a vacuum-tight manner by a cover glass 5. A focusing system for laser beams, shown here diagrammatically as a condensing lens 7, lies against the cover glass 5 outside the housing 1, preferably over a layer 6 of an immersion liquid. By means of this focusing system the electromagnetic radiation or laser radiation in the region of the sample of solid organic material denoted by the reference numeral 8 is focused in such a way that a small region of the said sample is evaporated and ionised. The ionised and negatively charged sample constituents are attracted by an electrode 9 at a high positive voltage and located opposite the sample 8. The ionised sample constituents pass from the electrode 9 to a mass spectrometer, not shown, whose mass separation system may conveniently be a time of flight tube. So that only the sample 8 and not also the cover glass 5 is evaporated, a spacer, e.g. a grid 10, is provided, whose thickness may be a few tens of microns. The sample may also be mounted between two grids.

By means of the apparatus shown in Figure 2, liquids or even gases can be investigated by the methods of the present invention. As an example, a chromatograph 11 is shown diagramatically, from which the substances to be investigated and which are dissolved in a carrier fluid pass into a line 13 provided with a metering valve 14. In order to be able to introduce this fluid into the vacuum chamber 1, a transporting strip 15 is provided. In this embodiment the strip 15 is unwound from a foller 16 and wound onto a roller 17. Locks 19 and 20 are provided in order to introduce and remove the strip 15. A layer (dotted line 21) of the substance applied to the transporting strip 15 is ionized by means of laser light pulses. A side arm 22 with a connecting flange 23 which is covered with a disc 24 transparent to laser light is provided on the side of the chamber 1. The lens system 7 serving to focus the laser light is located externally of the side arm 22. The lens system 7 and the plane of the window 24 are dimensioned and aligned in such a way that the focal point of the laser light is located where the axis 25 of the time of flight tube intersects the transporting strip 15. By means of such a device the sample 21 can also be bombarded in incident light. The nega-

tive ions thereby formed are attracted in the direction of the time of flight tube in the manner already described.

The described embodiment is essentially suitable for analysing liquid samples, but gaseous samples can also be absorbed on the strip 15 and thereby introduced into the vacuum chamber 1. In addition, there is also the possibility of spraying liquid or gaseous samples directly into the vacuum chamber in the region of the focal point of the laser light. This can, for example, take place discontinuously, in synchronisation with the laser light pulses.

It has proved particularly advantageous if the laser light has a wavelength of 265 nm and a pulse duration of 15 ns. In this way a power density of approx. 10^9 watts/cm^2 can be produced at the focal point. The analysed volume is approx. 10^{-12} cm^3.

CLAIMS

1. A method of analysing an organic substance which comprises exposing a sample of organic substance to laser radiation to evaporate and ionise a region of the sample, and passing the negative ions produced to a mass spectrometer.

2. A method of analysing an organic substance contained in the eluate leaving a chromatograph, which comprises exposing a sample of the eluate to laser radiation to evaporate and ionise a portion of the organic substance in the sample, and passing the negative ions produced to a mass spectrometer.

3. A method according to Claim 1, wherein the substance is a solid.

4. A method according to claim 1, wherein the substance is a liquid.

5. A method according to Claim 1, wherein the substance is a gas.

6. A method according to any one of the preceding claims, wherein the mass spectrometer is a time of flight mass spectrometer.

7. Apparatus for carrying out the method according to any one of the preceding claims, comprising a vacuum chamber, and means for introducing a sample of the organic substance to be investigated into the vacuum chamber, a mass spectrometer having components mounted in the chamber, a laser means for focusing the laser light onto the sample, and an electrode positively charged with respect to the sample for attracting in the direction of the mass spectrometer the negative ions produced by the bombardment of the sample with laser light pulses.

8. Apparatus according to Claim 7, wherein the means for introducing the substance to be investigated into the vacuum chamber comprise a transporting strip.

9. Apparatus according to Claim 7 or 8, wherein the mass spectrometer components mounted in the chamber include the time of flight tube of a time of flight mass spectrometer.

10. The use of mass spectroscopy of negative ions produced by laser beams, to analyse organic substances.

11. The use of mass spectroscopy of negative ions produced by laser beams, to analyse organic substances leaving a chromatograph.

12. Apparatus for analysing organic substances constructed, arranged and adapted to operate substantially as hereinbefore described with reference to the accompanying drawings.

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